

The University of Chicago

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REAGENTS TO UNSATURATED COMPOUNDS.
I. THE ADDITION OF HALOGEN ACIDS TO
VINYL CHLORIDE. II. ADDITION OF HY-
DROGEN BROMIDE TO 4, 4-DIMETHYL-
PENTENE-1. III. THE ADDITION OF
HYDROGEN IODIDE TO ETHYLENE
COMPOUNDS**

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1934

By
CHESTER WILBERT HANNUM

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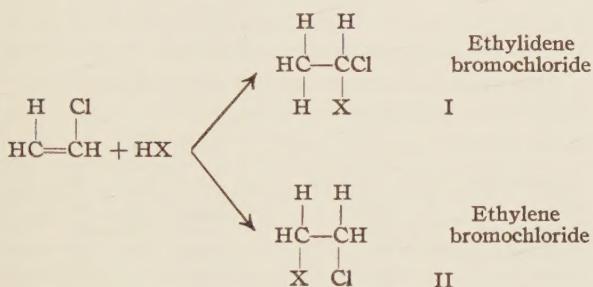


The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. I. The Addition of Halogen Acids to Vinyl Chloride

Introduction

In previous communications Kharasch and co-workers¹ demonstrated that the most important factor in the addition of hydrogen bromide to certain unsaturated substances was the peroxide content of the reaction mixture. It was shown that the "peroxide" effect could be overcome by good antioxidants in the absence of oxygen. An investigation was undertaken to determine to what extent "peroxides" influenced the addition of halogen acids to vinyl chloride.

The addition of halogen acid can occur according to scheme I or II



Under normal "non-peroxide catalyzed" conditions the formation of ethylidene bromochloride was found to occur exclusively as predicted.²

Previous Work on the Addition of Halogen Acids to Vinyl Chloride.—Very little work has been published on the addition of halogen acids to vinyl chloride. Wibaut³ found no addition between the two in the vapor phase while working with hydrogen chloride except when the reaction was catalyzed by the presence of certain metallic salts.

Factors Influencing the Addition of Hydrogen Bromide to Vinyl Chloride.—The "peroxide" content of the vinyl chloride-hydrogen bromide mixture is the most important single factor governing the direction and velocity of addition of hydrogen bromide to vinyl chloride. This behavior is similar to that of vinyl bromide, except that in our experience vinyl chloride is even

more sensitive to "peroxides" than allyl chloride, allyl bromide or vinyl bromide. This view is borne out by examination of Table I.

This table demonstrates that when attempts are made to remove all oxygen and peroxides by distillation and evacuation of the bomb tubes, the results are still the same as those noted with benzoyl peroxide, ascaridole, air, etc. In short, without a solvent or a good antioxidant the addition of hydrogen bromide to vinyl chloride leads to a rapid, nearly quantitative, formation of ethylene bromochloride. In the presence of metal catalysts, however, the peroxide effect is destroyed and nearly quantitative yields of the ethylidene bromochlorides are obtained.

TABLE I

THE ADDITION OF HYDROGEN BROMIDE TO VINYL CHLORIDE
IN ABSENCE OF ANTIOXIDANTS AND SOLVENTS AT ROOM
TEMPERATURE AND IN THE ABSENCE OF LIGHT

Agent added	Mml.	Air ^b	Reaction time, days	Yield, ^d %	1,1, %
None		+	3	87 ^a	1
None			3	77	0
Ascaridole	6.0	+	2	73 ^a	3
Benzoyl peroxide	4.1	+	2	79 ^a	0
Ferric chloride	1.2		1	76 ^a	87
(anhyd.)	1.2	+	1	42 ^a	100

^a Crude yield of isomers before distillation.

^b Bomb tubes sealed without evacuation and containing air. In all other runs the vacuum technique described by Mayo¹ was used.

^c All runs in this table were duplicated at least once.

^d Yields as given, except those labeled *a*, indicate calculated yields of bromochloroethanes after purification. Because of unavoidable and comparatively large losses in working with such small quantities of material (6.3 g. vinyl chloride), many runs credited with yields of 70–80% are undoubtedly quantitative. The column headed 1,1% gives % ethylidene bromochloride as determined by refractive index, the remainder being ethylene bromochloride.

The Effect of Antioxidants.—Table II summarizes the effect of antioxidants on the addition of hydrogen bromide to vinyl chloride *in vacuo* and in the absence of solvents. Good antioxidants in all cases formed mainly the "normal" addition product, ethylidene bromochloride. One weak antioxidant employed, *tert*-butylcarbylamine, was not as effective as the other antioxidants in producing the normal isomer but

(1) Kharasch and Mayo, *THIS JOURNAL*, **55**, 2469 (1933); Kharasch, McNab and Mayo, *ibid.*, **55**, 2521, 2531 (1933).

(2) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); Kharasch and Reinmuth, *J. Chem. Ed.*, **8**, 1703 (1931).

(3) Wibaut, *Rec. trav. chim.*, **51**, 636 (1932).

in conjunction with *p*-thiocresol or diphenylamine gave a product which was entirely ethylidene bromochloride. *tert*-Butylcarbylamine increases the velocity of the normal addition four- or five-fold.

Under influence of sun or artificial light, at room temperatures or near 0°, the effect of *p*-thiocresol and other antioxidants is almost completely destroyed. Strong illumination, particularly sunlight, increases tremendously the velocity of the "abnormal" reaction. Kharasch and his collaborators¹ have found that lowering the temperature during illumination decreases the magnitude of the peroxide effect in case of some substances. Due, however, to the greater susceptibility of vinyl chloride to peroxides we were unable to duplicate this effect at 0°. Lower temperatures were not investigated.

The addition of hydrogen bromide at elevated temperatures in the dark proceeds at an increased velocity but decreases the yield of "normal" product, showing the "peroxide" effect to be increased under these conditions. Manganese chloride *in vacuo* was found to have no effect on the course of the addition.

TABLE II

THE ADDITION OF HYDROGEN BROMIDE TO VINYL CHLORIDE IN VACUO IN ABSENCE OF SOLVENTS AT ROOM TEMPERATURE AND IN THE ABSENCE OF LIGHT
(EXCEPT AS NOTED IN REMARKS)

Added agent	Mml.	Reaction time, days	Yield, %	1,1, %	Remarks
<i>p</i> -Thiocresol	2.4	14	62	97	Washed vinyl chloride
<i>p</i> -Thiocresol	2.4	17	71	100	Unwashed vinyl chloride
<i>p</i> -Thiocresol*	1.6	5	50 ^a	19	
Thiophenol	3.6	14	54	93	
Diphenylamine	3.0	17	59	100	
<i>t</i> -Butylcarbylamine	2.1	4	93	80	
<i>t</i> -Butylcarbylamine and <i>p</i> -thiocresol	2.1 } 2.4 }	7	57	100	
<i>t</i> -Butylcarbylamine and diphenylamine	2.1 } 3.0 }	7	81	100	
Pyrogallol*	1.6	2	0	..	Red solid
<i>p</i> -Thiocresol	2.4	1	50	3	} 8 cm. from 500-watt lamp, 5°
<i>p</i> -Thiocresol	2.4	1.5	19	7	
<i>p</i> -Thiocresol	2.4	5	78	2	
<i>p</i> -Thiocresol	2.4	0.75	61	2	0° and sunlight
<i>p</i> -Thiocresol	2.4	3	77	19	76°
Diphenylamine	3.0	3	70	43	76°
Manganese chloride	1.0	2.5	70	2	

^a All materials must be freshly distilled *in vacuo* to be able to duplicate results consistently. It was found that a sample of *p*-thiocresol which was old and impure was rather ineffective as an antioxidant (*) but after purification by distillation *in vacuo* it behaved as an excellent antioxidant.

The Effect of Solvents.—Three solvents were used with and without antioxidants, namely, glacial acetic acid, nitrobenzene and mesitylene. We were able to form some 1,1 isomer, without the use of antioxidants, by causing the addition to proceed *in vacuo* in solvents such as nitrobenzene and particularly mesitylene. The addition of antioxidants to the solvents greatly increases the percentage of "normal" product, ethylidene bromochloride. In the presence of air, however, the solvent effect is of minor importance since the "peroxide catalyzed reaction" proceeds so fast that it obliterates quite effectively any antioxidant effect of the solvent.

The "peroxide" effect is accelerated by light to a tremendous extent, and only in the presence of good antioxidants may one obtain any appreciable yields of the "normal" addition product.

TABLE III

THE ADDITION OF HYDROGEN BROMIDE TO VINYL CHLORIDE IN THE PRESENCE OF SOLVENTS AT ROOM TEMPERATURE

All solvents in vacuum bombs distilled *in vacuo* before use; 5 cc. of solvent used per run.

Agent added	Mml.	Solvent	Air	Light	Re-action time, days	Yield, %	1,1, %
None		HAc		None	12	83	3
<i>p</i> -Thiocresol	2.4	HAc		None	12	56	77
Diphenylamine	3.0	HAc		None	15	65	44
None		HAc		500W	1	74	5
<i>p</i> -Thiocresol	2.4	HAc		500W	1	46	35
None		Nitrobenzene		None	32	71	29
<i>p</i> -Thiocresol	2.4	Nitrobenzene		None	12	54	77
Diphenylamine	3.0	Nitrobenzene		None	15	59	81
None		Nitrobenzene	+	None	6	84	2
None		Mesitylene		None	32	31	95
<i>p</i> -Thiocresol	2.4	Mesitylene		None	14	31	100
Diphenylamine	3.0	Mesitylene		None	18	38	97
None		Mesitylene	+	None	6	76	2

Factors Influencing the Addition of Hydrogen Chloride to Vinyl Chloride.—We find that no appreciable addition of hydrogen chloride to vinyl chloride occurs under peroxide-containing or peroxide-free conditions or upon illumination with light. We found, as did Wibaut,³ that addition occurs only under the influence of metallic salt catalysts such as ferric chloride and then ethylidene chloride was formed exclusively.

The Addition of Hydrogen Iodide to Vinyl Chloride.—The addition of anhydrous hydrogen iodide to vinyl chloride occurs rapidly in peroxide-containing or peroxide-free mixtures to give pure ethylidene chloriodide as indicated by the sharp boiling point of the addition product corresponding to that given in the literature for the 1,1 isomer. The refractive indices of all runs were

identical which, together with a common boiling point (114–115°), indicates a common product. The same products are obtained at –40° in the dark although addition at this temperature is quite slow. The strongly reducing hydriodic acid⁴ destroys all peroxides even at –40°, giving the “normal” addition product, ethylidene chloriodide.

TABLE IV

THE ADDITION OF HYDRIODIC ACID TO VINYL CHLORIDE

Added agent	Mml.	Air	Reaction time, days	Yield, ^b %	1,1, %
None		+	0.5	31	100
None ^a		+	2	15	100
None ^a			3	1	..
Benzoyl peroxide	0.8	+	0.5	100	100
Ascaridole	3.0	+	2	91	100
Benzoyl peroxide ^a	0.8	+	30	77	100
<i>p</i> -Thiocresol	2.4		4	84	100
<i>p</i> -Thiocresol ^a	4.8		30	10	100

^a Tubes stored in liquid ammonia (–40°) during addition.

^b Yield data rather inaccurate due to method of loading bomb tubes at liquid air temperatures.

Experimental Part

The vinyl chloride used was distilled as needed from a tank of the material kindly furnished through the courtesy of the Union Carbide and Chemical Co. It was sufficiently free from peroxides as indicated by the test with ferrous ammonium sulfate–ammonium thiocyanate as previously described.¹ To ensure uniform results, however, it was passed through a wash tower of dilute acetic acid and ferrous iron (to decompose any small amount of peroxides contained in the material), and then dried by passing through a large tube filled with calcium chloride and condensed in the bomb tube. The technique of addition was identical with that used by Kharasch and Mayo.¹

Hydrogen bromide was prepared by the method described in previous articles.¹ The bomb tubes used were of Pyrex glass of 21 mm. o. d. and 2 mm. wall. A trace of manganese chloride was added to all mercaptans used as antioxidants due to the action of this salt in catalyzing the oxidation of organic sulfur compounds. The bomb tube system was evacuated with a 3-stage mercury pump. The pressures obtained were 10^{–4} mm. or less. In all of the experiments 0.1 mole of vinyl chloride and 0.15 mole of hydrogen bromide were used. In the case of hydrogen iodide we used 0.12 mole of the halogen hydride.

(4) The addition of hydrogen iodide to many unsaturated substances is under way in this Laboratory to determine the extent and validity of this assumption.

In working up the crude reaction product the bomb was chilled at –80°, the top cracked off with a hot wire, the contents drowned in water, washed with weak alkali and water, vacuum distilled, dried, distilled at atmospheric pressure and the refractive index taken at 20°. As the index of refraction of the two isomers was found to be a linear function of composition, the amount of each isomer in the addition product was easily obtained. The refractive index of the bromochlorides and chloriodides of ethane are not given in the literature, but by fractionation of a mixture of the two bromochloro isomers through a Hempel column we obtained each isomer in a pure state. The fractions were refractionated and the refractive index of the largest portion taken as the refractive index of the pure isomer. The following constants were obtained.

	B. p. (735 mm.), °C.	n_D^{20}
Ethylene bromochloride	104–105	1.4908
Ethylidene bromochloride	80.5–81.5	1.4660

The ethylene bromochloride was identified by refluxing, with aniline to form the *N,N'*-diphenylethylenediamine m. p. 63.5–64°. The ethylidene bromochloride was decomposed by heating with moist silver oxide in a bomb tube for five hours at 100° and identifying the acetaldehyde formed as the 4-nitrophenylhydrazone of m. p. 127°.

Summary and Conclusions

1. It has been shown that under well-defined conditions hydrogen bromide can be added to vinyl chloride to give either 100% ethylidene bromochloride or 100% ethylene bromochloride.

2. It has been demonstrated that an oxygen or “peroxide” effect is responsible for the formation of ethylene bromochloride.

3. The addition of hydrogen iodide to vinyl chloride under peroxide-containing or peroxide-free conditions forms only ethylidene chloriodide.

4. The addition of hydrogen chloride to vinyl chloride in the absence of metal salt catalysts does not proceed at a sufficiently rapid rate to be studied conveniently.

5. The effects of solvents, light, temperature, antioxidants, metallic salts, and different halogen acids on the velocity and direction of the addition have been evaluated.

II. ADDITION OF HYDROGEN BROMIDE TO 4,4-DIMETHYLPENTENE-1

The addition of halogen acids to substituted ethylenes has been under investigation in our laboratory for some time, particularly as regards the effects of peroxides and antioxidants on the direction of addition. For certain theoretical reasons these studies included the addition of halogen acids to 4,4-dimethylpentene-1.

In view of the recent publication of Whitmore and Homeyer [*J. Am. Chem. Soc.*, **55**, 4555(1933)] it appears desirable to publish some of our pertinent findings.

Our results indicate that the direction of addition of hydrogen bromide to 4,4-dimethylpentene-1 is governed by the peroxide content of the material or reagents. From that standpoint the compound 1-bromo-4,4-dimethylpentane, the product first isolated by Whitmore and Homeyer, is what we define the "abnormal" product of the reaction. This product is formed whenever the addition of halogen acid is carried out in air, or when the mixture contains peroxides. On the other hand, if the addition of hydrogen bromide is carried out *in vacuo* in the presence of good antioxidants, the isomeric 2-bromo-4,4-dimethyl-

pentane is obtained. It is this last product that we consider the "normal" product of the reaction.

In conformity with what we have just stated, we find that if the addition of hydrogen bromide to 4,4-dimethylpentene-1 is carried out *in vacuo* (instead of in air) 50% of the 2-bromo-4,4-dimethylpentane is obtained. The physical constants of the hitherto unknown 2-bromo-4,4-dimethylpentane are: b. p. 59.4° at 34 mm.; n_D^{20} 1.4463; while those of the 1-bromo-4,4-dimethylpentane under the same experimental conditions are: 68.8° and 1.4485. The table summarizes some of our results. The yields were excellent in all cases.

No.	Mole of olefin	Mole HBr	Reagent added, in mole
1	0.046	0.075	Ascaridole, 0.0012
2	.046	.075	None
3	.045	.079	Acetic acid, 0.075
4	.048	.077	<i>p</i> -Thiocresol, 0.0024
5	.049	.088	Diphenylamine, 0.0030

No.	Gas in bombs	n_D^{20}	2-Isomer, % $\pm$ 10%
1	Air (R. T.)	1.4483	0
2	Vac. (0°)	1.4474	50
3	Vac. (0°)	1.4479	27
4	Vac. (R. T.)	1.4469	73
5	Vac. (R. T.)	1.4463	100

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. III. The Addition of Hydrogen Iodide to Ethylene Compounds

Introduction

Previous studies in this Laboratory on the addition of hydrogen bromide to ethylene compounds under carefully controlled conditions have indicated that the controlling factor guiding the addition to the double bond was the peroxide content of the reaction mixture.¹ However, simple experiments with peroxide containing unsaturated compounds demonstrated that hydrogen iodide is an excellent reagent for decomposing organic peroxides. It appeared very likely, therefore, that the addition of hydrogen iodide to ethylene compounds should not be affected by peroxides, and that under all conditions the "normal" addition product should be formed.

Previous Work.—Very little work has been recorded on the addition of anhydrous hydrogen iodide to ethylene compounds studied by us. The earlier investigators² are in agreement that isopropyl iodide is the only product of reaction between propylene and hydrogen iodide. Butene-1 has been treated with aqueous hydrogen iodide³ and found to form secondary butyl iodide. Whitmore and Homeyer⁴ report that neopentylethylene did not add hydrogen iodide to the double bond at 0°, when the olefin was saturated with hydrogen iodide, although hydrogen bromide under those conditions gave practically quantitative yields of 1-bromo-4,4-dimethylpentane.⁵

(1) Kharasch and Mayo, *THIS JOURNAL*, **55**, 2469 (1933); Kharasch, McNab and Mayo, *ibid.*, **55**, 2521 (1933); Kharasch, Hannum and Gladstone, *ibid.*, **56**, 244 (1934); Kharasch and Hannum, *ibid.*, **56**, 712 (1934); Kharasch and Hinckley, *ibid.*, **56**, 1212, 1243 (1934).

(2) Berthelot, *Ann.*, **104**, 184 (1857); Erlenmeyer, *ibid.*, **139**, 228 (1866); Butlerow, *ibid.*, **145**, 275 (1867); cf. Michael, *Ber.*, **39**, 2138 (1906).

(3) Wurtz, *Ann.*, **152**, 23 (1869).

(4) Whitmore and Homeyer, *THIS JOURNAL*, **55**, 4555 (1933).

(5) Cf. Kharasch, Hannum and Gladstone, Ref. 1.

The addition of hydrogen iodide to allyl bromide has never been described. Simpson⁶ reports having prepared the 1-bromo-2-iodopropane by the addition of an aqueous solution of bromoiodine to propylene. His product boiled at 160–168° with decomposition. It is quite evident that the structure of Simpson's compound has not been definitely established.

General Procedure of this Work

In this work anhydrous hydrogen iodide was added in equal molar quantities to the olefin in order to minimize any reduction of the iodide thus formed. The general technique of addition was the same as described in previous papers.¹ When bombs were run with peroxides such as terpene peroxide, ascaridole, etc., these substances were added to the olefin at least thirty minutes before the addition of the hydrogen iodide.

The reaction of olefins with hydrogen iodide is quite vigorous at room and even at low temperatures. The hydrogen iodide used by us was purified very carefully and, when cooled in liquid air, was always obtained in an absolutely white form entirely free of iodine. Table I summarizes briefly the results of our addition of hydrogen iodide to a number of unsaturated compounds. As stated, the only product of the reaction under peroxide and antioxidant conditions was the "normal product," the product analogous to that obtained under antioxidant conditions with hydrogen bromide. Under our method of addition there was not the slightest difficulty in adding the hydrogen iodide to neopentylethylene. The addition of hydrogen iodide to that molecule is ex-

(6) Simpson, *J. Chem. Soc.*, **27**, 564 (1874).

TABLE I^a

Olefin	Moles of olefin	Agent added	Moles of agent	Moles of HI	Technique	Reaction time, hours	Addition product Yield, %	B. p., °C.	Refractive index 20(D)
Propylene	0.069	Ascaridole	0.0012	0.073	Air	6	76	89-89.2	1.4985 ^b
Propylene	.079	Diphenylamine	.0029	.084	Vacuo	4.5	79	89-89.2	1.4985 ^b
Butene-1	.049	Ascaridole	.0012	.048	Air	3	52	119.5-119.8	1.4998 ^c
Butene-1	.079	Diphenylamine	.0029	.079	Vacuo	3	73	119.5-119.8	1.4991 ^c
Neopentylethylene	.049	Ascaridole	.0012	.054	Air	2	92	57.6(15 mm.)	1.4892 ^d
Neopentylethylene	.048	Diphenylamine	.0029	.048	Vacuo	20	60	57.6(15 mm.)	1.4891 ^d
Neopentylethylene	.049		...	.048	Vacuo	2	83	57.6(15 mm.)	1.4892 ^d
2-Iodo-4,4-dimethylpentane	.022		...	.044	Air	18 (0)	68	57.6(15mm.)	1.4895 ^d
Allyl bromide	.081	Ascaridole	.0012	.088	Air	2	81	66.2(20 mm.)	1.5908 ^e
Allyl bromide	.082	Ascaridole	.0012	.082	Air	6 (-38)	59	66.2(20 mm.)	1.5914 ^e
Allyl bromide	.070	Diphenylamine	.0029	.075	Vacuo	2	12		1.5900 ^f
Allylbromide	.100	Diphenylamine	.0029	.100	Vacuo	2 (0)	16 (40%) (60%)		1.5867 ^f 1.5896 ^f
Allyl bromide	.100	Diphenylamine	.0029	.100	Vacuo	5 (-38)	0		1.4671 ^g

^a All the additions described in this table were carried out in the dark. The purity of the starting materials was checked, whenever possible, by boiling point and index of refraction. In the case of propylene and butene-1, the materials were purified by careful fractionation. ^b Index of refraction corresponds to isopropyl iodide. ("I. C. T.," n_D^{20} 1.4997) n -propyl iodide n_D^{20} 1.5051. ^c Index of refraction corresponds to *s*-butyl iodide as prepared by us. This index is not recorded in the literature. ^d Index of refraction corresponds to 2-iodo-4,4-dimethylpentane. This experiment proves that hydrogen iodide has no effect on the product formed by the interaction of neopentylethylene and hydrogen iodide. ^e The material was 1-bromo-2-iodopropane. ^f Some 1-bromo-2-iodopropane and a large quantity of low boiling material (65-85° at 760 mm.). ^g Unchanged allyl bromide.

tremely rapid both in the presence of antioxidants *in vacuo* and in the presence of peroxides. The final product in both cases was the 2-iodo-4,4'-dimethylpentane.⁷

As far as the addition of hydrogen iodide to propylene, butene- and 4,4'-dimethylpentene is concerned, the peroxides *apparently* have no effect on the speed or direction of addition. However, our work with allyl bromide indicates that while hydrogen iodide decomposes peroxides, yet these substances have definite effects on the velocity of addition although they may not influence the direction of addition. Thus, at room temperature (two hours) or at -38° (six hours) excellent yields of the addition product of hydrogen iodide to allyl bromide were obtained in the presence of peroxides. The low temperature of addition has the advantage in that no reduction products of the 1-bromo-2-iodopropane are formed, and the final mixture contains the dihalopropane and unchanged allyl bromide only. However, in the absence of peroxides and in the presence of antioxidants the formation of the dihalopropane is

seriously hindered. Thus, at -38°, in a vacuum and in the presence of diphenylamine, no addition of hydrogen iodide occurred, and the allyl bromide was recovered unchanged. At 0° and in the absence of peroxides a low yield of the dihalopropane was obtained together with much unchanged allyl bromide, a low boiling material and a great deal of tar. The only constituent of the low-boiling material which was definitely identified was isopropyl iodide.⁸ Furthermore, the yield of the dihalopropane decreased very rapidly as the temperature of addition was varied between 0 and 20°, and the quantities of tar and isopropyl iodide were increased.

The formation of the isopropyl iodide in the addition of hydrogen iodide to allyl bromide is in agreement with the observation of Malbot⁹ and that of Sorokin¹⁰ that isopropyl iodide is readily obtained when 1,2-dihalopropane is treated with hydrogen iodide.

The proof of structure of the 1-bromo-2-iodopropane, obtained by us, was made by the Gladstone and Tribe method.¹¹

(7) The structure of the iodo compound thus obtained was proved by converting the iodide into the corresponding mercury compound by the usual methods. The iodine in the mercury compound was then displaced by bromine by shaking the mixture with silver bromide. The melting point of the mercury compound thus obtained was 116°, and it did not depress the melting point of the mercury compound prepared from the addition product of hydrogen bromide to neopentylethylene under antioxidant conditions.

(8) The identification was made by refluxing the low boiling material dissolved in benzene, with a suspension of the silver salt of 3,5-dinitrobenzoic acid, and crystallizing the benzene soluble material from 80% alcohol. The ester thus obtained melted at 115-116°, and the melting point was not depressed when mixed with a known sample of that material.

(9) Malbot, *Ann. chim.*, [6] **19**, 355 (1890).

(10) Sorokin, *Z. Chem.*, **6**, 519 (1870).

(11) Gladstone and Tribe, *Ber.*, **7**, 364 (1874).

Summary

1. A study of the addition of hydrogen iodide to ethylenic compounds which are capable of forming "normal" and "abnormal" addition products with hydrogen bromide (depending on the "peroxide" content of the reactant mixture) has shown that only the "normal" product of addition is formed, even in the presence of peroxides.

2. The normal addition of hydrogen iodide is

assumed to be due to the reducing action of this halogen acid on organic peroxides.

3. It is noteworthy that "peroxides" even though they do not affect the direction of addition of hydrogen iodide to unsaturated compounds, increase the velocity of addition, and in the case of allyl bromide allow the isolation of an addition product, which without added peroxides is formed to a slight extent only.

